

**We claim:**

1. A method of making an optical information storage medium, the method comprising:

(a) disposing a polymerizable composition between a base and a covering layer, at least one of the base and the covering layer having a first relief pattern on a side facing the polymerizable composition;

(b) spinning the base, the polymerizable composition and the covering layer in a centrifuge to distribute the polymerizable composition;

(c) polymerizing the polymerizable composition while the polymerizable composition is distributed between the base and the covering layer to form a polymerized layer having a second relief pattern corresponding to the first relief pattern;

(d) separating the polymerized layer from the first relief pattern; and

(e) filling the second relief pattern with a fluorescent information storage material.

2. The method of claim 1, wherein:

the polymerizable composition is photopolymerizable in light having a photopolymerizing wavelength;

the covering layer is transparent to the photopolymerizing wavelength; and

step (c) comprises applying the light having the photopolymerizing wavelength to the polymerizable composition through the covering layer.

3. The method of claim 2, wherein the polymerizable composition comprises 20 wt% of 1,6-hexanediol diacrylate (HDDA), 35 wt% of ethoxylated<sub>10</sub> bisphenol A diacrylate, 20 wt% of epoxy novolac acrylate oligomer in HDDA, and 2 wt% of Darocure 1173.

5

4. The method of claim 2, wherein the polymerizable composition comprises 63 wt% of polyester acrylate, 37 wt% of styrene and 2 wt% of benzoin isobutyl ether.

10

5. The method of claim 2, wherein the polymerizable composition comprises 23 wt% of modified urethane triacrylate, 5 wt% of 2-(2-ethoxyethoxy)ethylacrylate, 15 wt% of monopropylene glycol acrylate, 57 wt% of propoxylated<sub>3</sub> trimethylopropane triacrylate, and 2 % of Irgacure 784.

6. The method of claim 2, wherein the polymerizable composition comprises 20% of oligocarbonate methacrylate (OCM-2), 80% of aliphatic urethane triacrylate with  $M_n=5000$ , and 2% of Irgacure 651.

15

7. The method of claim 6, wherein step (c) comprises using a photoinitiator comprising 2 wt% of phenanthrenequinone and 1 wt% of triethanolamine.

8. The method of claim 6, wherein step (c) comprises using a photoinitiator comprising 2 wt% of camphorquinone and 1 wt% of triethanolamine.

9. The method of claim 6, wherein step (c) comprises using a photoinitiator comprising 1 wt% of eosin B, 1 wt% of dibutylaniline and 2 wt% of Irgacure 651.

20

10. The method of claim 2, wherein the polymerizable composition comprises 50 wt% ethoxylated bisphenol A diacrylate, 10% pentaerythritol triacrylate, 40 wt% of tripropylene glycol triacrylate and 1wt% of Irgacure 1700.

11. The method of claim 2, wherein the polymerizable composition comprises oligocarbonate methacrylate, 1% of Irgacure 651 and 1% of Irgacure 1173.

25

12. The method of claim 2, wherein the polymerizable composition comprises 20 wt% of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) M.W. 70000, 50 wt% of 1,6-

5 hexanediol diacrylate, 30 wt% of 4-vinyl-1-cyclohexane 1,2-epoxide, 1 wt% of Irgacure 500, 2 wt% of UVI 6974 and 2 wt% of triarylsulfonium hexafluoroantimonate.

13. The method of claim 2, wherein:

the polymerizable composition comprises 10% of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 2% of polypropyleneglycol M.W. 400, 15 wt% of  
10 tripropyleneglycol divinyl ester, 15 wt% of trimethylolpropane triacrylate, and 58 wt% of oligocarbonate methacrylate (OCM-2, Alvar-M, Ltd.); and

step (c) comprises using a photoinitiator comprising 2% Irgacure 500 and 2% triarylsulfonium hexafluorophosphate.

14. The method of claim 2, wherein the polymerizable composition comprises 20  
15 wt% of diepoxide propyleneglycol M.W. 600, 30 wt% of bisphenol A epoxy acrylate, 50% of propoxylated, neopentyl glycol diacrylate, 1 wt% of Irgacure 149 and 1 wt% of Irgacure 261.

15. The method of claim 1, wherein step (e) comprises:

providing a filling composition comprising a fluorescent dye; and

20 filling the second relief pattern with the filling composition.

16. The method of claim 15, wherein the filling composition further comprises a polymerizable substance and a solvent.

17. The method of claim 16, wherein:

the polymerizable substance comprises bis(4-glycidylphenoxy)methane (80 wt%),  
25 1,2,7,8-diepoxyoctane (10 wt%) and neopentylglycol (10 wt%);

the fluorescent dye comprises rhodamine 6G; and

5

the solvent comprises 2-ethoxyethanol, 2-propanol and ethanol in proportion 2:2:1 (by volume).

18. The method of claim 16, wherein:

the polymerizable substance comprises bisphenol A diglycidyl ether (75 wt%), 1,4-cyclohexanedimethanol diglycidyl ether (5 wt%), and 1,2,7,8-diepoxyoctane (20 wt%);

10

the fluorescent dye comprises coumarin 314; and

the solvent comprises 2-ethoxyethanol, 4-hydroxy-4-methyl-2-pentanone, 2-propanol and ethanol in proportion 1:1:2:1 (by volume).

19. The method of claim 16, wherein:

the polymerizable substance comprises bisphenol A diglycidyl ether (70 wt%), 1,4-butanediol diglycidyl ether (15 wt%), bis(3,4-epoxycyclohexylmethyl) adipate (5 wt%) and neopentyl glycol ethohylate (10 wt%);

the fluorescent dye comprises coumarin 153; and

the solvent comprises 4-hydroxy-4-methyl-2-pentanone, 1-butanol, 2-propanol, ethyleneglycol and 2,2,3,3-tetrafluoro-1-propanol in proportion 1:1:2:1:0.5 (by volume).

20

20. The method of claim 16, wherein:

the polymerizable substance comprises diglycidyl-1,2-cyclohexanedicarboxylate (45 wt%), 3-[bis(glycidylloxymethyl)methoxy]-1,2-propanediol (45 wt%), poly(bisphenol a-co-epichlorohydrin), glycidyl end-capped ( $m_n = 480$ ) (2 wt%) and dipentaerythritol (8 wt%);

the fluorescent dye comprises rhodamine 6G; and

25

the solvent comprises 4-hydroxy-4-methyl-2-pentanone, 1-butanol, methylethyl ketone and ethanol in proportion 2:2:1:1 (by volume).

21. The method of claim 16, wherein:

5

the polymerizable substance comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (80 wt%), 3-diglycidyl-1,2-cyclohexanedicarboxylate (8 wt%), poly[(o-cresyl glycidyl ether)-co-formaldehyde] ( $m_n = 870$ ) (2 wt%) and poly(caprolactone) triol ( $m_n = 300$ ) (10 wt%);

the fluorescent dye comprises oxazine 1; and

10

the solvent comprises 4-hydroxy-4-methyl-2-pentanone, 2-methyl-3heptanone, 3-methyl-2-butanone and cyclohexanone in proportion 1:1:2:2 (by volume).

22. The method of claim 16, wherein:

the polymerizable substance comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (80 wt%), glycerol proxylate triglycidyl ether (0.1 wt%) and poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate) (9.9%);

the fluorescent dye comprises oxazine 1; and

the solvent comprises 2-ethoxyethanol, 1-butanol, 2-propanol and 3-methyl-2-butanone in proportion 4:4:2:1 (by volume).

23. The method of claim 16, wherein:

20

the polymerizable substance comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (90 wt%), poly(caprolactone) triol ( $M_n = 300$ ) (2 wt%) and poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate) (8%);

the fluorescent dye comprises oxazine 1; and

the solvent comprises 2-ethoxyethanol, 1-butanol, 2-propanol and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol in proportion 1:1:1:4 (by volume).

25

24. The method of claim 16, wherein:

5 the polymerizable substance comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (90 wt%), glycidyl methacrylate (2 wt%) and poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate) (8%);

the fluorescent dye comprises oxazine 170 and oxazine 1 in proportion 1:10 (by weight); and

10 the solvent comprises 2-ethoxyethanol, 1-butanol, 2-propanol and 1,1,1,3,3,4,4,4-octafluoro-2-butanol in proportion 1:1:1:2 (by volume).

25. The method of claim 16, wherein:

the polymerizable substance comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (10 wt%), 4-vinyl-1-cyclohexane diepoxide (70 wt%), poly(propylene glycol) diglycidyl ether ( $M_n=640$ ) (10 wt%), and glycidyl methacrylate (10 wt%);

the fluorescent dye comprises rhodamine 6G; and

the solvent comprises 4-hydroxy-4-methyl-2-pentanone, 1-butanol, 1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedione, and methylethyl ketone in proportion 2:2:1:1 (by volume).

20 26. The method of claim 16, wherein:

the polymerizable substance comprises ethylene glycol divinyl ether (85 wt%), di(ethylene glycol)divinyl ether (10 wt%) and trimethylolpropane trivinyl ether (5%);

the fluorescent dye comprises coumarin 334 and pyrromethene 567 in proportion 1:1 (by weight); and

25 the solvent comprises 2-ethoxyethanol, 2-butanol, 2-propanol, 1,1,1,3,3,4,4,4-octafluoro-2-butanol, 2,2,3,3-tetrafluoro-1-propanol in equal proportions (by volume).

27. The method of claim 1, wherein step (e) comprises:

5 providing a filling composition;

filling the second relief pattern with the filling composition;

covering the filling composition with a covering composition comprising a fluorescent dye; and

10 causing the fluorescent dye to diffuse from the covering composition into the filling composition.

28. The method of claim 27, wherein the fluorescent dye has a first rate of diffusion in the polymerized layer and a second rate of diffusion in the filling composition, the second rate of diffusion being higher than the first rate of diffusion.

29. The method of claim 28, wherein the fluorescent dye comprises oxazine 1.

30. The method of claim 29, wherein the filling composition comprises 3 wt.% of polyacrylic acid solution in a mixture of 80% ethyl glycol and 20% isopropanol.

31. The method of claim 29, wherein the filling composition comprises 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (80 wt%), glycerol proxylate triglycidyl ether (0.1 wt%) and poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate (9.9%).

20 32. The method of claim 1, further comprising:

(f) repeating steps (a)-(e) a plurality of times to form a plurality of information layers;

and

(g) adhering the plurality of information layers together to form the optical information storage medium as a multilayer medium.

25 33. The method of claim 32, wherein the polymerizable composition is doped with 3% Irgacure 1700.

5

34. The method of claim 32, wherein the polymerizable composition is doped with 4% benzoyl peroxide and 0.1% dibutylaniline.

35. An optical information storage medium made according to the method of claim

1.

36. An optical information storage medium made according to the method of claim

10

2.

37. A multilayer optical information storage medium made according to the method of claim 32.

09761647, 041201